On the efficient implementation of many-body theories

Thesis of Ph.D. dissertation

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Introduction

This dissertation collects some of the results from the past few years in the field of many-body theory, that we have obtained while working at the Laboratory of Theoretical Chemistry, Eötvös University.

Part of our work concerns perturbation theory, as applied to the electron correlation problem of atoms and molecules. Single-reference perturbation approach is an efficient method of quantum chemistry to describe the electron correlation of molecules at around equilibrium geometry. In many single-reference applications the coupled-cluster theory is preferred, due to its technical and conceptual simplicity, still single-reference perturbation theory is widely used. In the case where a multi determinantal function is needed for a qualitatively correct description of a molecular state, single-reference methods break down and multi-reference methods have to be applied instead.

To devise a multi-reference method showing acceptable properties from every respect, like extensivity, spin-adapted nature, numerical stability in cases when the zero-order states show (near) degeneracy, invariance to orbital rotations at least at the same level as the zero-order function etc., is far less straightforward than in the single-reference case. In the dissertation two multi-reference perturbation approaches are discussed. The presentation focuses on details of the implementation of the theories. We used an automatized algorithm both for deriving formulae and producing the FORTRAN source code.

For large precision benchmark calculations Full Configuration Interaction (Full CI) method is computed when attainable. Application of this method is limited by the exponential scaling of the calculation cost with the dimension of the problem. To reduce the calculation cost one may eliminate components of the wave function that we consider unimportant. In the dissertation a new CI algorithm is discussed where the selection of important components of the wave function is based on strategy which explores the determinants gaining a weight above threshold during the CI iterations.

Multiconfigurational perturbation theories

1. A state-specific multi-reference perturbation theory (MCPT) was developed, where the reference function is a linear combination of determinants of an arbitrary model space. The zero-order Hamiltonian describes the model space by biorthogonal vectors and the complementary space is expanded by single determinants. In this framework there is a large flexibility of choosing zero-order energies. Davidson-Kapuy and Epstein-Nesbet type zero-order energies were tested. The original version of theory (MCPT) contains a projection orthogonal to the reference function while the modified version

(SC2MCPT) does not contain such a projection. This latter version is size-consistent at second order in energy.

2. Code generating routines and scripts were written to implement the MCPT theories at third order, using an orbital driven algorithm. The code generated this way allows to perform calculations for system which are too large to treat with a configuration driven algorithm.

3. Test calculations have been performed on moderate size systems to explore the efficiency of MCPT theories. Results show that for practical applications of the MCPT theories improvements are necessary in two directions: i) The strong dependence of the results on the Fermi-vacuum should be eliminated. ii) Separation of the reference energy and the energy of the excited determinants has to be guaranteed. These problems are currenty being investigated in our laboratory

Multipartitioning many-body perturbation theory

Another perturbation approach extensively studied in the dissertation is the Multipartitioning Many-Body Perturbation Theory (MP MBPT) originally published by Zaitevskii and Malrieu. This is an effective Hamiltonian approach where the model space is defined by a complete active space. The terminology "multipartitioning" refers to the property that all determinants in the model space define a zero-order Hamiltonian. Zero-order Hamiltonians are diagonal on the determinantal basis and they are defined by one-particle ionization energies and electron affinities. This ensures that model states are energetically well separated from the complementary space thereby avoiding the intruder state problem. This is remarkable among the effective Hamiltonian theories.

The *genuine formulation* of MP MBPT applies one set of ionization potentials and one set of electron affinities for each determinant. It was previously shown that the *genuine formulation* is size-extensive at second order.

4. I have shown that the *genuine formulation* is not size-extensive at third or higher order. To keep the extensivity, the same set of ionization potentials and electron affinities have to be used for all model space determinants. We refer to this version of the theory as *simple formalism*.

Spin-adaptation of MP MBPT was already published previously by Zaitevskii and Malrieu, by a modification of the zero-order Hamiltonian.

5. I have recognized that MP MBPT violates spatial symmetry if there is symmetry-determined spatial orbital degeneracy among the active orbitals. We have modified the definition of the zero-order Hamiltonian to obtain a spin- and symmetry-adapted formalism while keeping the beneficial properties of the original theory.

6. I have shown that MP MBPT can be represented by the diagrams known from the multi-reference many-body approach. Differences originate from the different treatment of denominators.

7. The scaling of the energies with the number of particles was studied in the system at higher orders of different MP MBPT formulations with the following conclusions: The *simple formalism* is size-extensive at any order similarly to MR MBPT. The *spin-adapted* formalism may involve mathematically disconnected but physically connected diagrams, therefore the theory is size-extensive. Using localized orbitals the *spin-adapted* formalism is also size-consistent. In the *general symmetry-adapted* formalism disconnected diagrams may also appear, but they do not harm size-extensivity as far as the degeneracies of the active orbitals does not scale with the system-size. Using localized orbitals the *general symmetry-adapted* formalism can be also size-consistent provided that the symmetry do not connect orbitals at infinite separation.

8. We have shown that the application of the *general symmetry-adapted* formalism can be problematic for cases where the dimension of the symmetry determined degeneracy can change along a reaction path. In these cases one has to use the lowest symmetry to obtain a continuous potential energy surface.

9. The MP MBPT theory was implemented up to fourth order applying the automatic code generator tools originally developed for MCPT. We have introduced intermediers to improve the efficiency of the code.

10. Numerical test calculations show that the third and fourth order corrections give significant improvement to the second order results. The robustness against intruder states is demonstrated on systems like ethylene distortion and different geometries of BeH_2 molecule.

A Sparse Full-CI algorithm

Regarding computational time, the bottleneck of a Full-CI algorithm is the calculation of the effect of the Hamiltonian on a linear combination of determinants. It is a common feature of modern algorithms to separate the determinants into alpha and beta strings. Excitations performed by the Hamiltonian are also classified into alpha-alpha, beta-beta and alpha-beta cases and programed separately to achieve a significant improvement over earlier algorithms.

11. We have observed, that importance of the components of a Full-CI vector (i.e. weight above threshold) can be related to an importance of alpha and beta strings. This means that certain strings are more populated by the important determinants than others. Finding these strings can lead to a procedure where the length of the full-CI vector is considerable reduced without sacrificing the accuracy important for chemistry.

12. A strictly variational numerical algorithm was developed, which initially makes distinction between important an unimportant determinants according to the strings that they contain. At a given iteration step those determinants are allowed to gain non-zero coefficient in the wave function, which include a string that is important based on a perturbational argument. At the initial step, the FCI algorithm published by Olsen and his coworkers was also implemented.

13. The efficiency of the algorithm is demonstrated on numerical examples. In the largest calculation (N_2 molecule) the FCI space contained 10 billion determinants of which 200 million determinants were used to approximate the exact energy with the error in the order of micro Hartree.

Publications supporting the thesis

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15. Z. Rolik and M. Kállay:
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